

Storage Tank Threshold Emissions Theory

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Date: November 6, 2014

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Overview

The question raised in this paper is whether infrared (IR) gas-imaging cameras are sensitive enough to detect volatile organic compound (VOC) emissions from the perimeter vents of internal floating roof storage tanks (IFRT's) when the tanks are in good condition, or whether perimeter vent emissions can only be detected when the tanks need to be repaired. Field experience and the initial test data presented in this paper suggest the latter case, but not under all possible gas imaging conditions that might be encountered in the field.

Storage Tank Emissions Estimates

The VOC emission rates from tanks that are designed to control evaporative emissions are estimated using equations found in Chapter 7 of a U.S. Environmental Protection Agency (EPA) document entitled *AP-42, Compilation of Emission Factors, Volume 1, Stationary Area and Point Emission Sources*, which are used by storage tank owners and state and local air pollution control authorities to establish tank VOC emission limits for a facility's Clean Air Act permits and also for emissions inventory purposes. The AP-42 equations are based on some 20 years of testing by the American Petroleum Institute in collaboration with EPA, and take into account the VOC emission rates associated with various floating roof design characteristics. The AP-42 emissions estimates only apply to tanks that are in good condition. There are no equations for estimating emissions from defective tanks.

FLIR GF320⁷ Camera Threshold Sensitivity Testing

The American Petroleum Institute standard for IFRT perimeter vents is one square foot of opening per 32 feet of circumference (see, API 650 H.5.2.2). The author constructed a test vent with a 1 square foot rectangular opening designed to look like a typical IFRT perimeter vent and

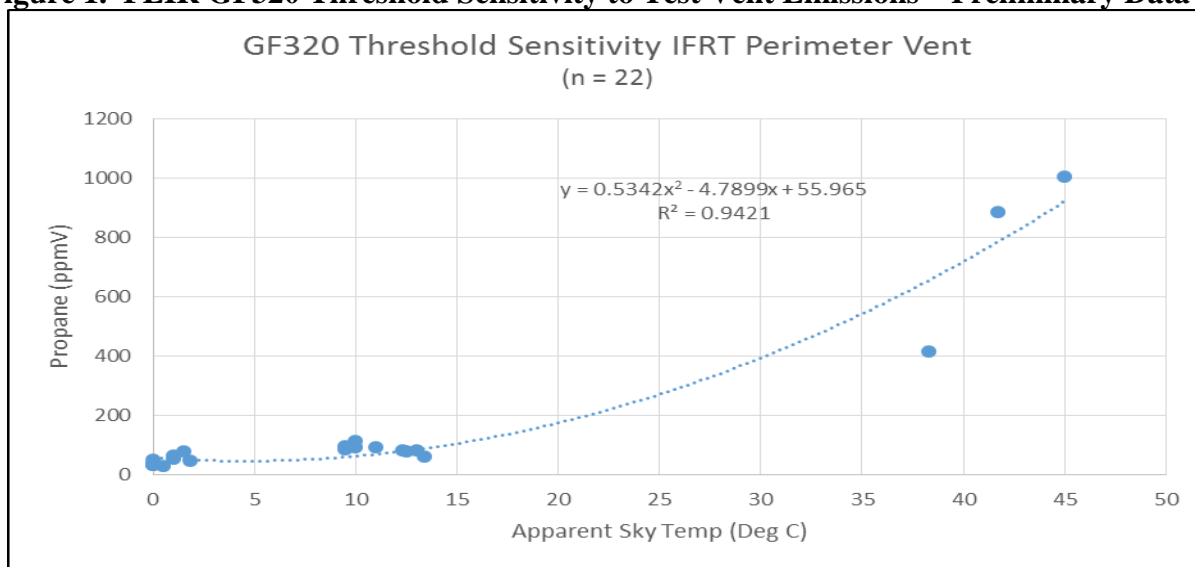
⁷ The FLIR GF320 camera is the make and model of gas-imaging cameras used by most EPA offices. Mention of the product is not intended to constitute product endorsement.

which can be operated so as to adjust the mass emission rate of an organic gas.⁸ Gas flow through the vent is provided by three tunneled fans (total flow rate = 0.85 m/s) and an internal flow-controlled gas distributor which is adjusted by the vent operator. The gas emission rate is based on the air flow rate and the one-minute integrated gas concentration readings at the vent outlet sampling tubes as measured using a flame ionization detector. The gas used for the testing was consumer-grade propane of the type used for barbeque grills.

The test vent was placed on the edge of a 22-foot high roof at the EPA Region III Environmental Science Center in Ft. Meade, Maryland, and also on a 24-foot high roof at the Denver Federal Center in Colorado, to provide a sky background for the vent observations.⁹ The emission rate of propane was gradually increased until an observer on the ground could just begin to see the propane emissions with a FLIR GF320 gas-imaging camera set on fully automatic mode.¹⁰ The camera's temperature spot-meter was activated so that the apparent sky background temperature, which affects gas-imaging contrast and thus sensitivity, could be recorded, and the observations were made when the winds were calm to light and variable. The objective was to determine the threshold sensitivity of the camera to propane emissions under optimum conditions, which can be scaled to other compounds such as benzene based on the relative infrared absorbance of the compounds within the IR spectrum (3.1 to 3.6 microns) detected by the camera.

As shown in Figure 1 below, the threshold sensitivity of the IR gas-imaging camera was affected by the apparent sky background temperature, which ranged 0° C to 45° C. The data indicates that the gas-imaging camera is much more sensitive to emissions when the sky background temperatures are low.

Figure 1. FLIR GF320 Threshold Sensitivity to Test Vent Emissions – Preliminary Data



⁸ IFRT perimeter vent dimensions vary by tank manufacturer and can be either rectangular or semi-circular. Rectangular vents are the most common based on the author's observations.

⁹ The height of large IFRT's is more typically in the range of 40 to 60 feet.

¹⁰ The sensitivity of the GF320 camera can be adjusted by the user or the camera can be set on Automatic mode. Automatic mode was selected to standardize the imaging sensitivity during the vent tests.

The estimated accuracy and precision of the test vent emission rate measurement is approximately $\pm 16\%$ based on the sum of the calibration gas certifications for the FID, the FID precision, and the flow rate uncertainty. Little difference in threshold sensitivity determinations was evident with different observers and gas-imaging cameras. However, even though wind speeds were very low during the tests, wind direction relative to the test vent flow direction appeared to affect the observer's ability to see emissions, with winds perpendicular to the vent flow having the most detrimental effect. Wind was likely a factor in the variability in the data at any given sky background temperature. More data will be collected in the 15° C to 30° C sky background temperature range which might require updating the equation shown in Figure 1.

Discussion

As noted above, the purpose of the vent testing was to determine whether a gas-imaging camera, in this case a FLIR GF320, is only sensitive enough to “see” VOC emissions from the perimeter vents of IFRT's that are emitting gases in excess of the AP-42 calculations and permit limits. For comparison purposes, Table 1 lists several tanks with various floating roof seals, contents, and estimated standing loss emission rates copied from tank operating permits issued by a state air pollution control agency.¹¹

Table 1. Example Large Internal Floating Roof Tank Emission Rates Per AP-42 Chapter 7

Floating Roof Seal Type	Contents	Calculated Standing Loss Emissions
Mechanical shoe with secondary wiper	Methanol	0.191 lbs/hr
Mechanical shoe with secondary wiper	Benzene concentrate	0.280 lbs/hr
Double wiper, vapor mounted	Pyrolysis gasoline	0.667 lbs/hr
Mechanical shoe with secondary wiper	Pyrolysis gasoline	0.667 lbs/hr

If, for example, emissions from the benzene tank listed in Table 1 came from three down-wind perimeter vents, then each vent would emit no more than 0.09 lb/hr (0.280/3) of benzene without there being a violation of the tank operating permit. By inference, emitting more than the permit limit could indicate that the tank is not in the good condition assumed when the emissions were estimated using AP-42, and the tank may therefore need to be repaired.

If benzene emissions were observed from the three downwind vents using a FLIR GF320 and the sky background temperature was 25° C, then based on the equation in Figure 1, the tank would theoretically be emitting benzene at a rate of at least 4.53 lbs/hr, adjusting for the difference in the sensitivity of the FLIR GF320 camera to benzene and propane on a ppmV basis.¹² The calculation is as follows:

$$\begin{array}{ll} \text{Benzene mol. wt.:} & 78.1 \text{ gmol}^{-1} \\ \text{Propane threshold sensitivity (Fig. 1):} & y = 0.5342x^2 - 4.7899x + 55.965 \end{array}$$

¹¹ “Standing loss” emissions from an IFRT are those that get past the floating roof seals and do not include “working loss” emissions during liquid withdrawal.

¹² The FLIR GF320's sensitivity to different gases is shown in Attachment 1.

Benzene relative absorbance coefficient: 0.36_{coeff} (volumetric basis)
Vent Flow Rate: 281 m³/hr

Calculation:

Eq. 1. Estimated benzene threshold sensitivity concentration at 25° C sky background:

$$y = 0.5342(25^\circ \text{ C})^2 - 4.7899(25^\circ \text{ C}) + 55.965 = 270.1 \text{ ppmV propane}$$
$$270.1 \text{ ppmV propane} \div 0.36_{\text{coeff}} = 750.3 \text{ ppmV benzene}$$

Eq. 2. Estimated benzene threshold mass sensitivity per unit volume:

$$\text{mg/m}^3 = [(750.3_{\text{ppmV}})(12.187)(78.1_{\text{gmol-l}})] \div 294^\circ \text{ K} = 2,429$$

Eq. 3. Estimate benzene threshold sensitivity emission rate:

$$2,429 \text{ mg/m}^3 * 281 \text{ m}^3/\text{hr} = 682,549 \text{ mg/hr} = 1.51 \text{ lb/hr per vent}$$

Eq. 4 Total estimated benzene tank threshold emission rate:

$$(3_{\text{vents}} * 1.51 \text{ lbs/hr threshold}) = 4.53 \text{ lbs/hr}$$

Under this scenario, the tank would be emitting benzene at a rate of about 16 times greater than the hourly permit limit if the emissions were observed at threshold sensitivity levels, and more so if the emissions appeared as a robust flow of gases from the vents.¹³

On the other hand, if the apparent sky background temperature was colder and in the range of 0° C, then the FLIR GF320's threshold sensitivity to benzene emissions would be 0.94 lbs/hr according to the equation in Figure 1, which is much closer to the permitted emission rate of 0.280 lbs/hr .

More sample runs with different sky background temperatures will be done in 2015 to better define the threshold sensitivity of the GF320 gas-imaging camera to tank vent emissions under a range of sky conditions. For example, the apparent sky background temperatures when the skies are clear during the warm season are commonly in the range of 15° C to 35° C. Threshold sensitivity test data is needed under those sky background conditions to fill a gap in the data presented here. However, the author believes that with more test data, it may be possible to use a FLIR GF320 gas-imaging camera to estimate the “at least” emissions from IFRTs.

¹³ AP-42 is used to estimate monthly emissions, not hourly emissions which are extrapolated for permitting purposes. There is debate about whether hourly emissions can be extrapolated from monthly estimates. However, given static operation, the author would not expect very large differences in the extrapolated hourly versus observed emissions from tanks that are in good condition.

Conclusion

One way that EPA inspectors use IR gas-imaging cameras to screen IFRT's for emissions problems is to compare tanks that are in static operating status to see if standing loss VOC emissions are emanating from the perimeter vents of one tank but not from others of similar design and liquid contents. This paper offers for further consideration the potential for an additional means of screening tanks when the threshold propane emission rate from a test vent at a given sky background temperature is known, and the emitted compound IR absorbance coefficient relative to propane is known. The observer would then be able to estimate what the VOC emission rate must be, at a minimum, in order to see the gas with a FLIR GF320, which can then be compared with the tank operating permit limit or estimated emissions as calculated using AP-42 Chapter 7. If the estimated "at least" emission rate is much greater than the permit emissions limit or AP-42 calculation, then one may have additional cause to undertake a detailed, up-close inspection of the tank.

Acknowledgements

The author thanks EPA employees Doreen Au, Sue Datson, Sounjay Gairola, Ken Garing, Martha Hamre, Anthony Miller, Matthew Schneider, and Tammy Stein for their expertise and participation during the vent emission rate testing. The author also thanks Mr. Zach Hedgpeth, P.E., EPA Region 10 for his thoughtful comments on a draft of this paper.

An update to this paper may be available in late 2015 by contacting Mr. Cary Secrest, USEPA, at secrest.cary@epa.gov.

Attachment

Attachment 1. Integrated spectral absorbance and propane relative response factors.

Compound	Absorbance Integration Scaled to FLIR Response	Response Factor Normalized to Propane
1,3-butadiene	0.009	0.26
1,3,5-trimethylbenzene	0.034	0.95
Acetic Acid	0.003	0.08
Acetaldehyde	0.004	0.12
Acetone	0.007	0.21
Acetylene	0.000	0.01
Acrylic Acid*	0.002	0.05
Benzene	0.013	0.36
Butane	0.043	1.21
Butene	0.025	0.70
Carbon tetrachloride	0.000	0.00
Dimethylformamide	0.019	0.53
Ethanol	0.019	0.53
ETBE	0.048	1.35
Ethylbenzene	0.030	0.84
Ethylene	0.006	0.17
Formaldehyde	0.007	0.18
Heptane	0.064	1.80
Hexane	0.057	1.61
Isoprene	0.016	0.45
MEK	0.017	0.47
Methane	0.011	0.30
Methanol	0.016	0.44
Methyl chloride	0.006	0.15
Methylene chloride	0.001	0.03
MTBE	0.045	1.25
m-Xylene	0.027	0.76
Octane	0.072	2.00
o-Xylene	0.027	0.75
Pentane	0.051	1.43

(Continued)

Compound	Absorbance Integration	Response Factor Normalized to Propane
Pentene	0.024	0.68
Propane	0.036	1.00
Propene	0.015	0.42
p-Xylene	0.029	0.80
Styrene	0.015	0.42
Toluene	0.020	0.56
Vinyl chloride	0.001	0.03
Water	0.000	0.00
Propane+Butane	0.039	1.10

* The spectra for Acrylic Acid was only available from PNNL at 50°C, versus 25°C as will all other gas spectra listed here.

Comparison of Empirical Pollutant Absorbance (temperature-based) at 1% Concentration versus Calculated Propane Relative Response Factors.

Compound	Empirical Absorbance at 1%	Empirical Response Factor Relative to Propane	Theoretical Response Factor Relative to Propane	% RPD
Propane+Butane	3.280	1.06	1.10	3.7
Ethylene	0.630	0.20	0.17	19.9
Methane	0.754	0.24	0.30	20.4
Propane	3.084	1.00	1.00	N/A

Source: *Spectral Testing of Gas-Imaging Cameras and Spectral Library*, Eastern Research Group, January 14, 2014. Electronic copies are available by contacting Mr. Cary Secrest, U.S. EPA, at secrest.cary@epa.gov. Note that the integrated absorbance for ethanol was added to the table after the above-referenced report was published.